

## MEETING MINUTES

SUBJECT: "POTENTIAL FOR EXOTHERMIC CHEMICAL REACTIONS IN WASTE TANKS"

TO: Those Listed		BUILDING Room A-210, 2750E		
FROM: W. W. Schulz		CHAIRMAN W. W. Schulz		
DEPARTMENT-OPERATION-COMPONENT	AREA	SHIFT	DATE OF MEETING	NUMBER ATTENDING
Research & Engineering	2750E	1	April 15, 1983	4

1. ATTENDEES:

W. W. Schulz (Rockwell) - Chairman  
 G. A. Beitel (Rockwell)  
 H. H. Van Tuyl, Jr. (PNL)  
 J. V. Robinson (PNL)

2. PURPOSE - BACKGROUND - REFERENCES

This meeting was held at the request of J. H. Roecker to determine first-hand the concerns of H. H. Van Tuyl regarding "Potential for Exothermic Chemical Reactions in Waste Tanks." The latter set of words is the title of a recent 8 page write-up voluntarily sent by Van Tuyl to Rockwell Hanford Operations (see Attachment 1). Van Tuyl's write-up makes substantial reference to earlier laboratory work and analyses made by George Beitel.

The goal in our April 15 meeting was to define specific Van Tuyl concerns and to agree, if possible, on recommended follow-on action(s).

3. MEETING DETAILSa. Reasons for Van Tuyl February 3, 1983 letter

Van Tuyl felt obliged to state why he wrote his February 3, 1983 letter. He said the thoughts voiced in this letter arose during organization and writing of a recent PNL report on "Assessment of Single-Shell Tank Residual Liquid Issues." Van said a decision was made by PNL not to put his material in the subject report but to submit it in writing to DOE-RL and Rockwell Hanford.

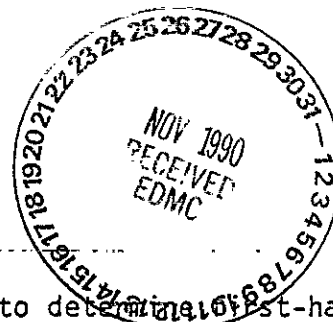
Van said his concerns about whether or not proper attention had been given (by Rockwell) to the presence of ferrocyanide precipitates in some single-shell tanks were of long-standing (25 years) and stemmed from his own personal involvement in the 1955-1960  $^{137}\text{Cs}$  scavenging program and his knowledge of laboratory-detonation (see Item c below).

b. Organic Materials in Single-Shell Tanks

An important early outcome of our meeting was that Van Tuyl is not concerned about possible exothermic reactions involving the small amounts of organics in salt cakes, sludges, and residual liquids in single-shell tanks. Van says he supports Beitel's earlier work and conclusions about the small likelihood of the occurrence of exothermic reactions caused by organic materials in such tanks.

c. Organic Materials in Double-Shell Tanks

By far, the bulk of the organic materials in the tanked wastes is in the double-shell tanks. In particular, special attention focuses on three million gallons of complexed concentrate which contain significant concentrations of such organic compounds as EDTA, HEDTA, citrate, and hydroxyacetate.



T00034

Meeting Minutes - "Potential for Exothermic Chemical Reactions in Waste Tanks"

April 15, 1983

Page 2

Van Tuyl is concerned that he does not find in any safety analyses (or other appropriate manuals, etc.) exact operating procedures for what we (Rockwell) would do if a potential exothermic run-away organic decomposition reaction were to occur. Van Tuyl correctly notes that organic decomposition (i.e., slurry growth = decomposition of HEDTA) reactions have been observed to occur in some waste tanks.

Van Tuyl wonders what might happen in the double-shell tanks as we continue to store wastes containing large amounts of various organic materials. Very likely, he says, we can safely continue the present storage mode indefinitely. But, we need to flag out safety checks if we change the storage system, e.g., change the  $\text{NO}_3^-/\text{NO}_2^-$  ratio, etc.

After some further discussion we concurred that the following actions should be implemented or considered:

- Establish, in writing (if it does not now exist), specific procedures to be followed in the event of evidence for an exothermic organic decomposition reaction(s) in a double-shell tank.
- Conduct appropriate laboratory analysis studies to establish what potentially hazardous (e.g., detonation, etc.) reactions involving organic materials are possible in the double-shell tanks.
- Determine what controls (i.e., dilution with water  $\text{NO}_3^-/\text{NO}_2^-$  ratio, etc.) can be used to mitigate or prevent organic decomposition reactions.

d. Ferrocyanide Precipitation in Single-Shell Tanks

In 1955-56 plant-scale precipitations of  $\text{Ni}_2\text{CsFe}(\text{CN})_6$  and  $\text{Ni}_2\text{CsFe}(\text{CN})_6 - \text{Sr}_3(\text{PO}_4)_2$  were performed in U-plant to remove  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  from aged  $\text{BiPO}_4$  process wastes. These scavenging operations were performed as part of the process of recovering uranium from stored  $\text{BiPO}_4$  wastes. The ferrocyanide precipitates were allowed to settle out in some single-shell tanks while the decontaminated supernate liquid was disposed of to the BC crib. H. Van Tuyl (also this author) were involved in laboratory-scale studies of the ferrocyanide scavenging process.

Because of his earlier involvement with ferrocyanide scavenging Van Tuyl has several concerns about the continued storage and eventual disposal (in-situ) of the ferrocyanide sludges. Specifically he asks

- Do we know which tanks contain the ferrocyanide sludges?
- What is the history of the tanks in which the ferrocyanide precipitates were laid down?, i.e., transfers in and out, other, solids, etc.
- Why doesn't our safety literature address stability of ferrocyanide precipitates?

Van Tuyl noted that some time in the 1950's (he wasn't sure exactly when) one of his laboratory co-workers (E. McClanahan) observed a ferrocyanide precipitate to detonate upon heating. Van Tuyl didn't remember all the details and said

71000394

the incident wasn't documented. He cites this experience, however, as an example of a potential exothermic reaction which could, under some circumstances, occur. Van speculates that ferrocyanide-nitrate detonation reactions may occur if triggered off by occurrence of some heat-evolving reactions in the tank.

Concerning stability of ferrocyanide sludges we concurred that a reasonable course of action would be to:

- ~~Incorporate appropriate words, if they are not there already, in documents, manuals, etc. which deal with continued safe storage of ferrocyanide sludges in single-shell tanks.~~
- Conduct literature reviews to determine thermal behavior of ferro- and ferricyanide precipitates and mixtures of such precipitates with solid nitrate salts.
- Conduct (or have conducted by outside contractor, e.g., Hazards Research, Inc.) thermal analysis (i.e., Sealed DTA) of mixtures of ferrocyanide solids and typical single-shell tank salt cake and sludge components, individually or mixtures thereof. Such tests would likely, it is believed, set extreme temperature boundaries for occurrence of exothermic reactions of ferrocyanide precipitates.

#### SUMMARY - RECOMMENDATIONS FOR FOLLOW-ON ACTION

- Van Tuyl is concerned about:
  - Stability of ferrocyanide precipitates in some single-shell tanks.
  - Lack of specific written procedures to deal with possible run-away organic decomposition reaction in double-shell tanks.
- Van Tuyl is not concerned about possible exothermic reactions involving small amounts of organic in single-shell tanks.
- Concerning organics in double-shell tanks the following actions should be implemented/or considered:
  - Document specific procedures to be followed in the event of any evidence for an exothermic organic decomposition reaction.
  - Conduct analyses and laboratory studies to establish what potentially hazardous reactions involving organic materials are possible.
  - Determine what controls can be used to mediate or prevent organic decomposition reactions.

- Concerning ferrocyanide precipitates in some single-shell tanks the following actions should be taken or considered:
  - Establish which tanks contain such sludges and quantities thereof.
  - Document awareness of possible safety considerations in continued storage or disposal of ferrocyanide sludges.
  - Conduct literature reviews to determine thermal behavior of ferrocyanide precipitates and mixtures of such precipitates with solid nitrate salts.
  - Conduct differential thermal analyses (DTA) of mixtures of ferrocyanide precipitates and typical single-shell tank salts, sludges, and liquid components.

POTENTIAL FOR EXOTHERMIC CHEMICAL REACTIONS IN WASTE TANKS

H. H. Van Tuyl

February 3, 1983

Background

Organic chemicals have been added to Hanford waste tanks, particularly as ferrocyanides and when processing sludges at B Plant. Recent planned or ongoing activities involving stored wastes have possibly increased the potential for reaction of these wastes with nitrate salts in the waste tanks. Risk evaluations appear to be deficient in assessing the consequences of a deflagration, and in determining the probability of either a deflagration or detonation. The present question is whether current plans and recent safety-related documentation have given proper consideration to the available information about organic compounds in waste tanks.

The principal organic additions to Hanford waste tanks<sup>1</sup> are 1200 tonnes of "organic carbon" and 500 tonnes of  $\text{Ni}_2\text{Fe}(\text{CN})_6$ . Analyses<sup>2</sup> of total organic carbon in certain waste tanks have shown up to 11 M total organic carbon (p. 50) in solution, and Tank 104-T is reported to contain 10.2 weight percent total organic carbon in "water insoluble" material (p. 51). These numbers are the maximum values for carbon concentration of which I am aware.

An early hazards evaluation<sup>3</sup> called attention to the cyanide problem (pages 7, 12, 17-19). It stated on p. 18, "A tank sampling program could be used to determine the presence or absence of cyanide. If it were found to be present, an experimental laboratory program aimed at determining the specific chemistry of the hazard would be justified. As the first step in evaluating this possible problem, it is recommended that a sampling and analytical program be commenced to determine the presence or absence of cyanide in TK-241-BYR-101. In addition, potential input wastes to the 101 Tank should be sampled and analyzed for cyanide." I am not aware of the existence, nature, or results of such a program.

A later preliminary safety analysis<sup>4</sup> noted on p. 14 a maximum permissible salt cake temperature of 260°C, and stated, "Prior to evaporation, a representative sample of the contents from each tank will be collected, dried,

and heated to temperatures of 260°C to assure that no significant exothermal reactions occur." The exothermic reaction of principal concern in this study was decomposition of ammonium nitrate. The means of assuring a "representative" sample were not discussed.

A 1980 assessment of risks<sup>5</sup> states on p. 42, "Self-Explosion (Chemical)". This event represents an explosion of the mixture in the tank. The basic constituent is sodium nitrate, and there is a very small admixture of organic material. Powerful explosives can be made by mixing proper proportions of organics and sodium nitrate, but this is not possible here because there is too little organic material with respect to the sodium nitrate. There is also no way to reach the detonation temperature of 400°C (Beitel, 1977). The release estimate is that <1% of the tank contents would be expelled to air in the form of respirable particles." It also addressed (p.31) a thermal excursion without identifying the source or rate of temperature rise. The thermal excursion is identified (p. 99) as the initiating event with highest product of frequency and consequence.

Another 1980 report on technical status of environmental aspects of waste management<sup>6</sup> did not refer to organics at all based on my rapid examination of a microfiche copy in the library.

Another 1980 report<sup>7</sup> described a reaction observed in Tank 241-SY-101 between dissolved oxidants and organic material, reported to have occurred in April 1977.

#### Explosion Studies

Kenneth A. Gasper of Rockwell Hanford Operations was recently requested to supply copies of reports about organic constituents in tanks and reactions that occur when they dry. He supplied the following:

T.C. Goodale, "Test Summary, The Sensitivity of Nuclear Waste to Detonation," Stanford Research Institute, PYD 3339, August 13, 1975.

Letter, December 15, 1975, L. E. Bruns to G. L. Hanson, "Explosion and Fire Hazards Associated with Z-9 Top Sediments Removal".

G. A. Beitel, "Sodium Nitrate Combustion Limit Tests," Atlantic Richfield Hanford Company, ARH-LD-123, April 1976.

G. A. Beitel, "Final Report on Investigation of Stability of Organic Material in Salt Cake," Atlantic Richfield Hanford Company, ARH-LD-126, April 1976.

The first item<sup>8</sup> describes two series of tests with sodium nitrate or simulated salt cake and various organic materials. The first series (2" dia. x 5" long) showed no detonation. The second series (6" dia. x 15" long) led the author to state, "We concluded that the ionized waves observed in the second series of tests could have been detonation waves, their low velocities being accounted for by the low energy of the detonation reaction per gram of sample."

The second item refers to the top Z-9 crib sediments, and is only of peripheral interest to waste tank concerns.

The third item by G. A. Beitel<sup>9</sup> includes useful background (pages 2-4) on combustion, deflagration, and detonation. Beitel states on p. 4, "the fact that a small quantity will not support combustion does not prove that the large mass will not support combustion." Related to some experiments with simulated salt cake rather than pure  $\text{NaNO}_3$ , he observes on p. 13, "These effects were most likely due to the presence of  $\text{NaNO}_2$ , which is more unstable (reactive) than  $\text{NaNO}_3$  even though it has a lower oxidizing power." One of the recommendations he makes (p. 22) is, "Additional information should be obtained on the pressure dependence of paraffin or resin combustion with  $\text{NaNO}_3$ . One-kg samples in sealed, pressure-limited containers should be tested with a variety of compositions at pressures of one to 100 atmospheres. Again, such tests have the potential of being destructively explosive and would require the respect accorded to similar quantities of TNT."

The fourth item, also by Beitel<sup>10</sup>, refers on p. 1 to the SRI tests (item 1 above) and states, "No evidence of detonation was seen in any of the samples, a finding in agreement with the literature which states that black powder (a nitrate plus charcoal type explosive) is shock insensitive (cannot be triggered by a shock wave)." This statement seems to be at variance with the statement quoted above from the SRI report.

3  
1  
10  
1  
5  
0  
2  
1  
1  
6

A detonation is an unlikely but severe event. The studies discussed above leave uncertainties about the effects with cyanides, effects of scale, and possible role of sodium nitrite. Cyanides were not a part of the study. Scale-up from 2" dia. to 6" dia. changed from no observed effect to a possible low order detonation, but no extrapolation is made to the actual size of waste tanks. Sodium nitrite is observed to be more unstable than sodium nitrate, but the potential effects are not fully analyzed.

Although there are still some uncertainties about detonation, the studies do serve to answer the concerns about salt cake containing homogeneously distributed organics at less than one weight percent. They do not answer questions at higher organic contents, such as sludges (e.g. ferrocyanide precipitates) or the concentrated organic materials which may deposit from solutions.

#### Exothermic Reactions

A recent article by David W. Smith<sup>11</sup> describes runaway reactions and thermal explosions, based on thermodynamic data, kinetic parameters, and physical properties. Two observations are especially pertinent: (1) "Typically for a runaway situation (e.g., a polymerization), there is an induction period with slow 'slipping away' of temperature control; then after reaching a certain temperature, the reaction apparently takes off." and (2) "a critical volume (or critical radius) exists for the product or reaction mixture for each temperature above which a thermal runaway reaction or decomposition must occur."

My concerns are that a slow, apparently controlled temperature increase may become a runaway reaction, and that the large system size (a million gallon test tube) may cause the reaction to occur at a lower temperature than would be predicted based solely on observations in much smaller systems.

The observed reaction<sup>7</sup> in Tank 241-SY-101 apparently occurred when one component of the organic material (HEDTA or hydroxyethyl ethylenediamine triacetic acid sodium salt) was partially oxidized, involving only two of the ten carbon atoms. Other organic components and the balance of the HEDTA were apparently not affected. No problems resulted from this reaction of organic matter with oxidants, but the reaction is expected to be exothermic and accelerating with increasing temperature. If the rate of the reaction had



been greater by either having a shorter half time or by involving a greater fraction of the total organic carbon, then the tank temperature could have increased appreciably. The important points are that a reaction of organic complexant with oxidizing salts has been observed, that the reaction was

~~unexpected, and that the rate or extent of reaction was not known~~ beforehand. If corrective action (such as dilution) were necessary to control the reaction rate, it is doubtful that adequate information is available to the tank farm operators to assure prompt and correct remedial action.

Winters<sup>2</sup> identifies organic complexants actually added to wastes amounting to 2.2 kilotons of organic, and states, "These complexants represent only about 1% of the total weight of the waste inventory but may be as high as 24% of the B Plant and Purex waste." Actual measurements of total organic carbon in waste tanks are quoted by Winters as up to 11M total organic carbon in solution, and up to 10.2% by weight as insolubles. At 11M carbon, a solution would contain 500 g of carbon per gallon. The salts in the solution are largely nitrates or nitrites, which provide the oxidizing power for causing the organic carbon to explode.

Beitel<sup>9</sup> studied propogation of combustion through various mixtures of sodium nitrate or salt cake with charcoal, paraffin, resin and sugar. The most reactive materials were sugar and charcoal. When sugar was mixed with salt cake, it gave "violent combustion" with 25 wt% sugar, "very slow" reaction with 15 wt% sugar, and no combustion with 10 wt% sugar. Beitel's tests with sugar were apparently limited to an 8 mm dia. tube. He reports comparative tests for other materials in 8 mm and 16 mm dia. tubes, with consistently more vigorous combustion in the larger sized tubes. The minimum weight fraction of sugar required to sustain combustion in a large vessel cannot be estimated from his data. He did not study any of the complexants listed in Winters<sup>2</sup> as having been added to waste tanks.

Citric and tartaric acids are chemically similar to sugar, and might be expected to behave similarly in reactions with sodium nitrate. Winters<sup>2</sup> states that  $3.3 \times 10^6$  moles (about 634 tons) of citric acid have been added to the waste, and he uses tartaric acid as a component of his synthetic feed. Thus, appreciable amounts of easily oxidized organics are likely to be present in waste tanks, along with much larger amounts of organics which are more difficult to ignite but which burn with a greater energy per gram of fuel.

## Potential Consequences

Beitel<sup>10</sup> states, "...one kilogram of detonating material could conceivably cause a waste tank dome to fail...". Thus, even one gallon of solution with 11M total organic carbon poses a potential threat to the integrity of a waste tank. Of course, a "trigger" must be available to release this energy by detonation in order for this small amount to cause a significant effect.

The quantity of organic material added per day while processing sludges at B Plant<sup>12</sup> is stated as 3.87 tons, based on 4,000 gallons of feed per day. If the waste were concentrated to a volume equal to the feed volume, a million gallon waste tank would correspond to 968 tons of organic material used in B Plant.

The existence of gross amounts of both organics and nitrates in waste tanks has been confirmed by analyses. Detailed studies have not been found which address the potential for releasing this energy at an undesirable rate, using either the major or the most unstable organics which are indicated to be present in the tanks. The actual composition of the organic in the waste tank is unknown; in fact, Winters<sup>2</sup> cites chemical analyses to account for only 2.2M carbon of the 7.4M which was observed in a particular tank, with the remainder being uncharacterized.

A 1964 hazards evaluation<sup>5</sup> states, "More than 100 tons of cyanide (calculated as cyanide ion) were added during the waste scavenging program and distributed among various tanks." It also adds, "Mixtures of solid salts at nitrate-to- $\text{Cs}_2\text{ZnFe}(\text{CN})_6$  mole ratios in the range of about 0.4 to 0.6, exploded when heated to approximately 350° C (660° F)." It is not stated whether this is the minimum ignition temperature under credible conditions.

One intriguing data point presented by Winters<sup>2</sup> is the 10.2 wt% water insoluble total organic carbon in Tank 104-T which is stated to contain "1st Cycle Bismuth Phosphate Sludge." This could represent ferro- and ferricyanide precipitates used for cesium removal. If so, there is a potential for a severe explosion in this tank if a suitable initiation source is ever present.

According to a recent study<sup>5</sup> (as stated on pp. 82-83) the consequence of structural failure of a tank is 0.0014 potential latent fatal cancers (PLFC) and the consequence of a chemical explosion throughout a tank is 43 PLFC.

This might help to place the physical consequences in perspective. However, the consequences with regard to future funding or to public perception are not quantified.

#### Reaction Probabilities

Initiation of a combustion reaction requires a significant source of heat. This may be supplied conventionally or by a detonation wave. A detonation wave could be provided by an explosive compound such as nitrated organics or heavy metal azides (possible decomposition products of hydrazine). The more likely initiating event would be thermal initiation of a reaction of an easily oxidized organic (e.g., citrates or tartrates), which would provide enough heat to initiate reaction of more stable organics. The latter materials would react throughout the tank as either a deflagration or detonation depending on conditions.

A side observation is that the existence of significant quantities of organic materials in waste tanks does not provide data on the probability of exothermic reactions. It does provide data on the maximum consequences of exothermic reactions. Probability is dependent on presence of an initiating event, and changes in any parameter may alter this probability. For example, changes in moisture content may be extremely important. It would be much easier to estimate the probability of an initiating event if it were known what conditions were required for the initiating event.

The most recent report by Beitel that I have found<sup>13</sup> says on page 8, "Although sodium nitrite may be present and is more reactive than sodium nitrate, it is less energetic and to the extent it is present, reduces the worst possible hazard." While this is true, the presence of sodium nitrite may be expected to increase the probability of an initiating event.

One data point exists. An unexpected exothermic reaction between organics and waste did occur, even though it had no significant impact. The next unexpected event may not be so benign. Statistics do not permit estimation of the time to next failure or the magnitude of the next failure. Is it prudent to assume this risk without further studies?

## REFERENCES

1. Technical Aspects of Long-Term Management Alternatives for High-Level Defense Waste at the Hanford Site, RHO-LD-141 (1980) Rockwell Hanford Operations, Richland, WA page 3-4.
2. W. I. Winters, Effect of pH on the Destruction of Complexants with Ozone in Hanford Nuclear Waste, RHO-SA-203, (June 1981) Rockwell Hanford Operations, Richland, WA 99352.
3. G. E. Backman et al., Chemical Processing Department, Hazards Evaluation, In-Tank Waste Solidification Project CAC-965, RL-SEP-65, (November 24, 1964) General Electric Company, Richland, WA 99352.
4. C. M. Unruh, A Preliminary Safety Analysis of Near Surface Storage of Radioactive Waste as Salt Cakes, BNWL-1194 (January 1970) Battelle Memorial Institute, Pacific Northwest Laboratories, Richland, WA.
5. D. J. Quinn et. al., An Assessment of the Risks Associated with Continued Storage of High-Level Waste in Single-Shell Tanks at Hanford, RHO-LD-55 (May 1980) Rockwell Hanford Operations, Richland, WA.
6. Technical Status Report on Environmental Aspects of Long-Term Management of High-Level Defense Waste, RHO-LD-139 (October 1980) Rockwell Hanford Operations, Richland, WA.
7. Calvin Delegard, Laboratory Studies of Complexed Waste Slurry Volume Growth in Tank 241-SY-101, RHO-LD-124 (December 1980) Rockwell Hanford Operations, Richland, WA.
8. T. C. Goodale, Test Summary, The Sensitivity of Nuclear Waste to Detonation, PYD 3339 (August 13, 1975) Stanford Research Institute, Menlo Park, CA.
9. G. A. Beitel, Sodium Nitrate Combustion Limit Tests, ARH-LD-123, (April 1976) Atlantic Richfield Hanford Co., Richland, WA 99352.
10. G. A. Beitel, Final Report on Investigation of Stability of Organic Material in Salt Cake, ARH-LD-126, (April 1976) Atlantic Richfield Hanford Co., Richland, WA 99352.
11. David W. Smith, "Runaway Reactions and Thermal Explosions," Chem. Eng. p.79-84 (Dec. 1980).
12. J. S. Buckingham, Waste Management Technical Manual, ISO-100, Chapter 6, (August 31, 1967) Isochem, Inc., Richland, WA 99352.
13. G. A. Beitel, Exothermic Potential of Sodium Nitrate Salt Cake, ARH-LD-163 (June 1977) Atlantic Richfield Hanford Co., Richland, WA.